STOCHASTIC ANALOGY OF ENTROPY OF A SYSTEM WITH A CHEMICAL REACTION

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On the basis of stochastic model of a reversible first-order reaction A $\rightleftarrows$ B, a function of an integer-valued random variable is introduced which can be considered as an analogue of the entropy due to chemical reaction (reaction entropy). The Ishida stochastic reaction entropy can be resolved into two terms the first of which corresponds to the mean ensemble value of introduced reaction entropy and the second one corresponds to a measure of information about the composition of the system.

The present work deals with a stochastic analogy of a function known from irreversible thermodynamics — entropy of a system due to first-order chemical reaction A $\rightleftarrows$ B (reaction entropy). The stochastic model of the reaction is based on common postulates of stochastic theory of chemical reactions[1-3] and represents the reaction as linear birth and death processes. It is assumed that the system has only one degree of freedom: its composition, characterized by the number of particles of the reactant A. The reaction entropy of the system changes therefore only if its composition is changed, *i.e.* if a chemical conversion takes place. In contrast to the previous Ishida's definition of the stochastic reaction entropy, first the stochastic system entropy as a function of composition is defined (*i.e.* as a function of an integer-valued random variable), and from this the ensemble average entropy as a continuous function of time is derived. It can be shown that in large systems the last quantity is actually equal to the entropy due to chemical reaction introduced in irreversible thermodynamics. The Ishida stochastic reaction entropy can be expressed as a sum of this dominant component and of another quantity which can be interpreted as a measure of information about the composition of the system.

Stochastic Description of a Reversible First-Order Reaction

We shall consider a closed reaction system of constant volume in contact with a large, constant-temperature bath. The system contains a constant total number of particles, N, which can exist in two forms, A and B; the probability that a particle A will be converted in a time interval $(t, t + \Delta t)$, $\Delta t \rightarrow 0$, into B is $k_1 \Delta t$, and the

probability that a particle B will be converted into A in the same time interval is $k_2 \Delta t$. We assume that the reaction does not alter the thermal equilibrium of the system. We denote the number of particles X at time t as N_X; if $N_A = j$, then $N_B = N - j$. The state of the system can be characterized by a single variable, *e.g.* number of particles A, N_A. This quantity is an integer-valued random variable characterized by the probability distribution

$$P_j(t) \equiv \text{Prob}\{N_A = j; t \mid N_A = N_A^0; t = 0\} ; \quad j = 0, 1, ..., N , \qquad (1)$$

where $P_j(t)$ fulfil the following system of differential-difference equations[1-3]:

$$dP_j(t)/dt = k_1(j + 1) P_{j+1}(t) + k_2(N - j + 1) P_{j-1}(t) -$$
$$- [k_1 j + k_2(N - j)] P_j(t) . \qquad (2)$$

If $P_j(0) = \delta_{N,j}$ (*i.e.* at time $t = 0$ is $N_A^0 = N$, $N_B^0 = 0$), then $P_j(t)$ is given by the binomial distribution[2,3-5]

$$P_j(t) = \binom{N}{j} [p_A(t)]^j [p_B(t)]^{N-j} , \qquad (3)$$

where

$$p_A(t) = \{k_2 + k_1 \exp[-(k_1 + k_2) t]\}/(k_1 + k_2) \qquad (4a)$$

is the probability that a randomly chosen particle will be in the form A at time t, and

$$p_B(t) = k_1\{1 - \exp[-(k_1 + k_2) t]\}/(k_1 + k_2) \qquad (4b)$$

is the probability that a randomly chosen particle will be in the form B at time t. It follows from the form of the distribution (3) that the mean number of particles at time t

$$\langle N_A \rangle \equiv \sum_{j=0}^{N} j P_j(t) = N p_A(t) \qquad (5a)$$

and the mean number of particles B at time t

$$\langle N_B \rangle \equiv \sum_{j=0}^{N} (N - j) P_j(t) = N p_B(t) \qquad (5b)$$

are identical with the deterministic values following from the mass action law if the constants k_1 and k_2 are considered identical with the deterministic rate constants of the isolated reactions A → B and B → A.

The variance of the number of particles A at time t is

$$D^2\{N_A\} \equiv \sum_{j=0}^{N} j^2 P_j(t) - (\sum_{j=0}^{N} j P_j(t))^2 = N p_A(t) \, p_B(t) = \langle N_A \rangle \, \langle N_B \rangle / N . \quad (6)$$

In the limit case for $t \to \infty$ (macroscopic equilibrium) we have

$$\lim_{t \to \infty} P_j(t) \equiv P_j^e = \binom{N}{j} K^{N-j}/(1 + K)^N , \quad (7)$$

$$\lim_{t \to \infty} \langle N_A \rangle \equiv \langle N_A \rangle_e = N/(1 + K) , \quad (8a)$$

$$\lim_{t \to \infty} \langle N_B \rangle \equiv \langle N_B \rangle_e = KN/(1 + K) , \quad (8b)$$

$$\lim_{t \to \infty} D^2\{N_A\} \equiv D_e^2\{N_A\} = KN/(1 + K)^2 = \langle N_A \rangle_e \, \langle N_B \rangle_e / N , \quad (9)$$

where $K = k_1/k_2$ is the equilibrium constant of the reaction and the subscript e refers to equilibrium.

Now, we shall consider a more general initial condition. Let $P_j(0) = \delta_{N_A^0, j}$; $0 \le N_A^0 \le N$, i.e. at time $t = 0$ is $N_A = N_A^0$ and $N_B = N - N_A^0 = N_B^0$. Then

$$P_j(t) = \sum_{i=0}^{j} \binom{N_A^0}{i} [p_A^{(1)}(t)]^i \, [p_B^{(1)}(t)]^{N_A^0 - i} \binom{N_B^0}{j-i} [p_A^{(2)}(t)]^{j-i} \, [p_B^{(2)}(t)]^{N_B^0 - j + i} , \quad (10)$$

where

$$p_A^{(1)} = \{k_2 + k_1 \exp[-(k_1 + k_2) \, t]\}/(k_1 + k_2) , \quad (11a)$$

$$p_B^{(1)} = k_1\{1 - \exp[-(k_1 + k_2) \, t]\}/(k_1 + k_2) , \quad (11b)$$

$$p_A^{(2)} = k_2\{1 - \exp[-(k_1 + k_2) \, t]\}/(k_1 + k_2) , \quad (11c)$$

$$p_B^{(2)} = \{k_1 + k_2 \exp[-(k_1 + k_2) \, t]\}/(k_1 + k_2) . \quad (11d)$$

The distribution (10), which is the solution of the system (2) with the initial condition $P_j(0) = \delta_{N_A^0, j}$, can be derived as follows: Since for a reaction of first order the possibility of conversion of one particle does not depend on the conversion of other particles, the particles of the system can be thought to be divided into two groups. The first group contains particles which were in the form A at time $t = 0$, the second contains particles which were in the form B at $t = 0$. The probability that the system contains j particles A at time t, $P_j(t)$, is given by the sum of products of the probabilities that the first group contains i particles A at time t and the second $j - i$ particles A; the summation refers to products for $i = 0, 1, ..., j$. The probability that a ran-

domly chosen particle in the r-th group will be in the form X at time t, $p_X^{(r)}$ ($r = 1$ or 2, X = A or B), is derived in the usual way[5]. Mean values of the number of particles A and B at time t corresponding to the distribution (10) are

$$\langle N_A \rangle = N_A^0 p_A^{(1)}(t) + N_B^0 p_A^{(2)}(t) \,, \tag{12a}$$

$$\langle N_B \rangle = N_A^0 p_B^{(1)}(t) + N_B^0 p_B^{(2)}(t) \,. \tag{12b}$$

Both mean values are again in accord with the deterministic solution. The variance of the number of particles A is

$$D^2\{N_A\} = N_A^0 p_A^{(1)}(t)\, p_B^{(1)}(t) + N_B^0 p_A^{(2)}(t)\, p_B^{(2)}(t) =$$
$$= \left(k_1^2 N_A^0 \langle N_A \rangle - k_2^2 N_B^0 \langle N_B \rangle\right)\left(N_A^0 - \langle N_A \rangle\right)/(k_1 N_A^0 - k_2 N_B^0)^2 \,. \tag{13}$$

Limit expressions P_j^e, $\langle N_A \rangle_e$, $\langle N_B \rangle_e$ and $D_e^2\{N_A\}$ corresponding to macroscopic equilibrium are also in this case given by Eqs $(7)-(9)$. As a special case, we shall consider the initial condition $N_A^0 = \langle N_A \rangle_e = k_2 N/(k_1 + k_2)$. Then the mean value of the number of particles A and B remains constant for any $t > 0$ and equal to the initial one, and only the variance changes. The time dependence of the variance of the number of particles A is in this case given by

$$D^2\{N_A\} = D_e^2\{N_A\} \left\{1 - \exp\left[-2(k_1 + k_2)\, t\right]\right\} \tag{14}$$

which for $k_1 = k_2 = k$ and $4kt \to 0$ gives

$$D^2\{N_A\} = Nkt = m \,, \tag{14a}$$

where m means the mean number of reaction events (conversions of particle A to B or B to A) in the interval $(0, t)$. This limit relation corresponds to modelling of short-time fluctuations of the number of particles A close to the deterministic equilibrium by a symmetric one-dimensional random walk[6].

Stochastic Analogy of Entropy of a System with Chemical Reaction A $\rightleftarrows$ B

Definition of stochastic system entropy. The first definition of stochastic entropy due to chemical reaction of the type A $\rightleftarrows$ B was proposed by Ishida[4]. The entropy can be according to irreversible thermodynamics[7] expressed as

$$S = -R[n_A \ln (n_A/n_A^e) + n_B \ln (n_B/n_B^e)] + S_e \,, \tag{15}$$

where R denotes gas constant, n_X molar concentrations of substances X = A or B

at time t, n_X^e concentrations in equilibrium and S_e the entropy of the system in equilibrium. In the deterministic sense, the concentrations are uniquely defined continuous functions of time so that Eq. (15) defines the entropy as a function of the composition and a unique function of time. Ishida's definition of the stochastic entropy is equivalent to replacing the concentrations n_X in (15) by their stochastic mean values, $\langle N_X \rangle$, which in terms of the distribution corresponds to the definition

$$S = k_B \sum_{j=0}^{N} P_j(t) \ln \left[P_j^e / P_j(t) \right] + S_e , \qquad (16)$$

where k_B denotes Boltzmann constant (in the stochastic definition, the composition of the system is expressed by the number of particles and not in mol units, therefore R is replaced by k_B). The sum on the right-hand side of equation (16) can be resolved into two terms: $k_B \sum_{j=0}^{N} P_j(t) \ln P_j^e - k_B \sum_{j=0}^{N} P_j(t) \ln P_j(t)$ (this resolution is similar to that of generalized H-function in statistical mechanics). In what follows, we shall analyse the properties of these two terms separately.

We shall define the quantity S_j, which we shall call the (stochastic) entropy of the system in the state $N_A = j$, as

$$S_j = k_B \ln P_j^e + c , \qquad (17)$$

where c is an unspecified constant. This equation is formally analogous to the Boltzmann relation between entropy and thermodynamic probability of state known from statistical mechanics[8]. The system entropy is by its definition related to the stationary distribution P_j^e and not to the distribution $P_j(t)$ (the connection between S_j and $P_j(t)$ is suggested in ref.[9]), since if the system persists in state j, its entropy must be constant. The quantity P_j^e can be considered as the probability of occupation of the state j obtained from a long-time observation of the system (*cf.* the definition of the probability of state in statistical physics[8,10]). The stochastic system entropy S_j thus defined is a function of the integer-valued random variable N_A and does not depend explicitly on time. For large values of j and $N - j$, P_j^e can be approximated with the use of the Stirling formula and S_j can be rewritten as

$$S_j = -k_B \big[j \ln \left(j / \langle N_A \rangle_e \right) + (N - j) \ln \left((N - j) / \langle N_B \rangle_e \right) \big] - \\ - \tfrac{1}{2} k_B \ln \left(2\pi j (N - j) / N \right) + c . \qquad (17a)$$

The value of S_j is maximum if j attains a value j^*, for which P_j^e is maximum. With increasing N, j^* approaches the mean value $\langle N_A \rangle_e$, and hence the theoretical value corresponding to the deterministic equilibrium.

From Eq. (*17*) we obtain immediately the fluctuation formula[8,11]

$$P_j^e = P_{j*}^e \exp \left[(S_j - S_{j*})/k_B \right] . \tag{18}$$

This can be interpreted as a relation between the probability of occupation of state j on a long-time average and the system entropy corresponding to this state. For large values of N we have $P_{j*}^e \approx (2\pi D_e^2 \{N_A\})^{-1/2}$, hence

$$P_j^e \approx (2\pi D_e^2 \{N_A\})^{-1/2} \exp \left[(S_j - S_{j*})/k_B \right] . \tag{19}$$

Since according to the DeMoivre–Laplace limit theorem the binomial distribution (*3*) can be for large N and $(j - j^*)^3/N^2 \to 0$ replaced by the normal distribution[12] we have for j not very different from j^*

$$S_j - S_{j*} \approx -k_B (j - j^*)^2 / 2D_e^2 \{N_A\} . \tag{20}$$

Mean ensemble entropy. The mean value of the quantity S_j with respect to the distribution $P_j(t)$, which we shall call the mean ensemble entropy at time t,

$$\langle S_j \rangle = k_B \sum_{j=0}^{N} P_j(t) \ln P_j^e + c , \tag{21}$$

is a continuous function of time and its value depends on $P_j(0)$. The mean ensemble entropy in equilibrium,

$$\lim_{t \to \infty} \langle S_j \rangle \equiv \langle S_j \rangle_e = k_B \sum_{j=0}^{N} P_j^e \ln P_j^e + c , \tag{22}$$

depends neither on time nor on the distribution at time $t = 0$. The sense of these mean values is connected with the idea of an ensemble of a very large number of systems which are at time $t = 0$ in the same state and in which a reaction proceeds under the same conditions. The relative frequency of systems in state j in the ensemble at time t is $P_j(t)$, and the mean value of the quantity, Y_j, depending on j, obtained by averaging over all systems of the ensemble, is $\langle Y_j \rangle = \sum_{j=0}^{N} Y_j P_j(t)$. With increasing t, the relative frequency of systems in state j approaches P_j^e and the ensemble is in the limit $t \to \infty$ described by the stationary distribution P_j^e. The mean value of Y_j in the limiting case for $t \to \infty$ is $\langle Y_j \rangle_e = \sum_{j=0}^{N} Y_j P_j^e$ and does not depend on t. It is denoted as the mean value of Y_j in equilibrium. The quantity $\langle Y_j \rangle_e$ can be, however, interpreted not only as the ensemble mean value but also as a time-averaged value obtained from a long-time observation of a single system.

It is obvious that $\langle S_j \rangle_e < S_{j*}$, *i.e.* the mean ensemble entropy in equilibrium is smaller than the maximum system entropy corresponding to the most probable state $j*$. This inequality is a consequence of the existence of fluctuations, hence a consequence of the probability character of the reaction. In the envisaged ensemble at any time t sufficiently far from the beginning of the reaction, not all systems are in the state $j*$ corresponding to the maximum system entropy. In large systems, there is a large number of states that are close to the most probable state $j*$ and are characterized by a value of P_j^e little smaller than P_{j*}^e; the system will be only rarely in the state $j*$ so that on a long-time average it will be only exceptionally in a state corresponding to the maximum entropy.

For large N, the distribution P_j^e in Eq. (22) can be replaced by the normal distribution and then it can be shown that

$$S_{j*} - \langle S_j \rangle_e \approx \tfrac{1}{2} k_B . \qquad (23)$$

The variance of the quantity S_j in equilibrium is for large N

$$\langle S_j^2 \rangle_e - \langle S_j \rangle_e^2 \approx \tfrac{1}{2} k_B^2 \qquad (24)$$

so that in the limiting case for $N \to \infty$ we have the inequality

$$S_{j*} - \langle S_j \rangle_e < \left(\langle S_j^2 \rangle_e - \langle S_j \rangle_e^2 \right)^{1/2} , \qquad (25)$$

i.e. the difference between the entropy of the system in the most probable state and the mean value of the entropy in equilibrium is smaller than the standard deviation of the quantity S_j in equilibrium.

We shall consider large N and $\langle N_X \rangle \gg 1$, X = A or B. Then it follows from Eq. (17a) by substituting the normal distribution for $P_j(t)$ that

$$\langle S_j \rangle - \langle S_j \rangle_e \approx -k_B \big[(\langle N_A \rangle + \tfrac{1}{2}) \ln (\langle N_A \rangle / \langle N_A \rangle_e) +$$
$$+ (\langle N_B \rangle + \tfrac{1}{2}) \ln (\langle N_B \rangle / \langle N_B \rangle_e) \big] - \tfrac{1}{2} k_B (N \, D^2\{N_A\} / \langle N_A \rangle \langle N_B \rangle - 1) . \qquad (26)$$

For $|\langle N_A \rangle - \langle N_A \rangle_e| \gg (D_e^2\{N_A\})^{1/2}$, only the first term in this equation need be considered and the difference $\langle S_j \rangle - \langle S_j \rangle_e$ approaches with increasing N the value given by Eq. (15) (where R is replaced by k_B and the mol units by the numbers of particles), *i.e.* the value derived in irreversible thermodynamics. In a special case, where the initial composition of the systems in the ensemble at time $t = 0$ is identical with the equilibrium one, the mean number of particles A remains constant and only the variance changes: $D^2\{N_A\}$ increases from zero to $D_e^2\{N_A\}$ (Eq. (14)). In this case

we have

$$\langle S_j \rangle - \langle S_j \rangle_e \approx -\tfrac{1}{2}k_B(D^2\{N_A\}/D_e^2\{N_A\} - 1) > 0 . \qquad (27)$$

This inequality results from the fact that the system which is at a certain moment in the most probable state passes during the subsequent change of state into a less probable one; the inequality (27) is therefore the result of fluctuations in the system. The decrease of the mean value $\langle S_j \rangle$ with time is in no relation to a macroscopic process ($\langle N_A \rangle$ is constant) and characterizes only a change in the distribution $P_j(t)$ caused by the fluctuations.

Therefore, for quite general initial conditions in the ensemble the inequality $\langle S_j \rangle - \langle S_j \rangle_e \leqq 0$ does not always hold but we have always

$$\langle S_j \rangle - \langle S_j \rangle_e \leqq S_{j^*} - \langle S_j \rangle_e \qquad (28)$$

since $\langle S_j \rangle \leqq S_{j^*}$ for any t and $P_j(0)$. The right-hand side of this inequality approaches $\tfrac{1}{2}k_B$ with increasing N.

A stochastic analogy of the basic equation of irreversible thermodynamics of chemical reactions for entropy production in the system during a change in composition

$$d_i S = (\mu_B - \mu_A)\, dn_A/T \qquad (29)$$

(μ_X denotes chemical potential of component $X = A$ or B, T temperature) can be seen in the equation

$$S_j - S_{j-1} = [\mu_B^0 + k_B T \ln(N - j + 1) - \mu_A^0 - k_B T \ln j]/T \qquad (30)$$

which applies for the stochastic system entropy (μ_A^0 and μ_B^0 are standard chemical potentials referred to one particle so that $K = \exp[(\mu_A^0 - \mu_B^0)/k_B T]$). For the mean ensemble entropy $\langle S_j \rangle$ we have the relation

$$d\langle S_j \rangle/dt = k_B \sum_{j=0}^{N} (dP_j(t)/dt) \ln P_j^e = k_B \sum_{j=0}^{N} \{k_1 j \ln[jK/(N - j + 1)] -$$
$$- k_2(N - j) \ln[K(j + 1)/(N - j)]\} P_j(t) \qquad (31)$$

and the time change of the quantity $\langle S_j \rangle$ cannot be expressed generally as an elementary function of $\langle N_A \rangle$. Under certain conditions, however, this equation can be approximated by a simple relation. If N is large then for such values of t for which $\langle N_X \rangle \gg 1$ and $|\langle N_X \rangle - \langle N_X \rangle_e| \gg (D_e^2\{N_A\})^{1/2}$, $X = A$ or B, we can write

$$d\langle S_j \rangle/dt \approx k_B \ln(\langle N_B \rangle/K\langle N_A \rangle)\, (d\langle N_A \rangle/dt) =$$
$$= (\mu_B^0 + k_B T \ln\langle N_B \rangle - \mu_A^0 - k_B T \ln\langle N_A \rangle)\, (d\langle N_A \rangle/dt) > 0 . \qquad (32)$$

It follows from the derived relations that the quantity $\langle S_j \rangle$ can be for large N and $\langle N_X \rangle \gg 1$, $|\langle N_X \rangle - \langle N_X \rangle_e| \gg (D_e^2\{N_A\})^{1/2}$, $X = A$ or B, identified with the entropy due to chemical reaction in irreversible thermodynamics. For a laboratory description of the reaction, it is suitable to introduce the degree of conversion of the component X, $x_X \equiv \langle N_X \rangle / N$, rather than the mean number of particles X. From the mentioned restrictions for $\langle N_X \rangle$ the restrictions for x_X follow: $x_X \gg 1/N$, $|x_X - x_X^e| \gg$ $\gg (D_e^2\{N_A\})^{1/2}/N = K^{1/2}/(1 + K) N^{1/2}$. It is obvious that if N is large, $\langle S_j \rangle$ can be considered identical with the entropy of irreversible thermodynamics in the whole experimentally accessible range of the variable x_X.

Entropy and the measure of information. Ishida's stochastic entropy defined by Eq. (*16*) involves the sum $\sum_{j=0}^{N} P_j(t) \ln P_j(t) \leq 0$, which can be interpreted as a measure of information of the observer about the composition of the given system. If at time $t = 0$ $P_j(0) = \delta_{N_A, j}$, then the value of this sum is maximum (*i.e.* zero); for any $t > 0$ its value is negative. If at time $t = 0$ we know with certainty that the composition of the system is $N_A = N_A^0$, then at time $t > 0$ we know only the probability distribution of the number of particles A. If we perform a measurement at time t showing that the system's composition is $N_A = j$, then the measure of information increases again to the initial (zero) value. The entropy of the system immediately before and after the measurement is constant (it is assumed that the hypothetical measurement requires only an infinitesimally short time and does not alter the state of the system), but the measure of information increases as a result of the measurement by the value of $-\sum_{j=0}^{N} P_j(t) \ln P_j(t)$. The deterministic description of the chemical reaction $A \rightleftarrows B$ corresponds formally to passing to a continuous variable j and to a distribution $P_j(t) = \delta(j - \langle N_A \rangle)$ (where δ denotes Dirac's delta function) maintaining the dependence of S_j on composition in the form of the limiting equation (*17a*) (precisely: of the highest first term on its right-hand side). In this case the information about the system's composition does not change in the course of the reaction since the composition at time t is determined by the initial condition, $N_A = N_A^0$, $t = 0$, uniquely; the entropy of the system, however, increases with time.

The quantity $\sum_{j=0}^{N} P_j(t) \ln P_j(t)$ can in general even increase with time. This can be illustrated as follows. Let $P_j(0) = \delta_{N,j}$ and N be large. Then for $\langle N_X \rangle \gg 1$, $X = A$ or B, we have

$$\sum_{j=0}^{N} P_j(t) \ln P_j(t) \approx -\tfrac{1}{2}[\ln (2\pi\, D^2\{N_A\}) + 1] \qquad (33)$$

and

$$(\mathrm{d}/\mathrm{d}t)\sum_{j=0}^{N} P_j(t) \ln P_j(t) \approx [\langle N_A \rangle - \langle N_B \rangle)/2\langle N_A \rangle \langle N_B \rangle] (\mathrm{d}\langle N_A \rangle/\mathrm{d}t). \qquad (34)$$

For $K \leqq 1$, $\langle N_A \rangle - \langle N_B \rangle$ is always positive, hence the right-hand side of *(34)* is negative. For $K > 1$, however, this side is positive if $\langle N_A \rangle < N/2$. We denote by $t_{N/2}$ the time for which $\langle N_A \rangle = N/2$; then $t_{N/2} = (k_1 + k_2)^{-1} \ln \left[2k_1/(k_1 - k_2) \right]$. The quantity $\sum\limits_{j=0}^{N} P_j(t) \ln P_j(t)$ decreases in the interval $(0, t_{N/2})$, at time $t_{N/2}$ attains its minimum equal to approximately $-\left[\ln (\pi N/2) + 1 \right]/2$ and increases in the interval $(t_{N/2}, \infty)$ to $\sum\limits_{j=0}^{N} P_j^e \ln P_j^e$. In the limit case $K \to \infty$, it increases again to the original zero value: the system will be at time $t \gg t_{N/2}$ almost certainly in the state $N_A = 0$; the distribution $P_j(t)$ approaches $\delta_{0,j}$ with increasing t.

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Translated by K. Micka.